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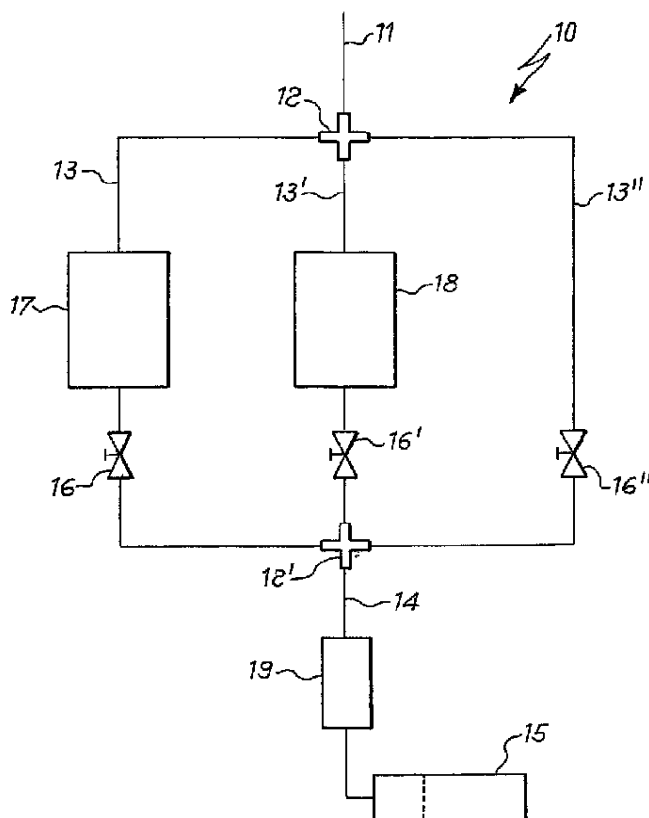
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(54) Title: METHOD AND SYSTEM FOR MEASURING OXYGEN AND WATER CONCENTRATION IN HYDROGEN  
THROUGH ION MOBILITY SPECTROMETRY



(57) Abstract: A method for the quantitative analysis of the oxygen and water content in hydrogen through ion mobility spectrometry is described, consisting in a ) carrying out a first measure on a hydrogen sample from which oxygen and water have been removed, in order to determine the contribution to the measure of water due to the "background" of the instrument; b) carrying out a second measure of oxygen concentration in the same hydrogen sample from which water has been removed; c) carrying out a third measure of the hydrogen sample, without any previous purification; d) comparing the three measures. A system for carrying out the method is also described.

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“METHOD AND SYSTEM FOR MEASURING OXYGEN AND WATER  
CONCENTRATION IN HYDROGEN THROUGH ION MOBILITY  
SPECTROMETRY”

5           The present invention relates to a method for measuring oxygen and water concentration in hydrogen through ion mobility spectrometry as well as to a system which allows carrying out the method.

          Hydrogen is a gas largely employed as a reagent gas in the integrated circuits industry. It is known that the purity of all the materials employed is  
10   essential in the manufacture of these devices; as a matter of fact, impurities possibly present in the reagents or in the reaction environment can be incorporated in the solid state devices, altering the electrical properties thereof and thereby leading to production wastes. The purity requirements of the gases used in the manufacture may vary depending on the manufacturer and on the specific process  
15   wherein the gas is employed. Generally, a gas is considered suitable for the manufacture when its impurity content is not higher than 10 ppb (parts per billion, that is, a molecule of impurity every  $10^9$  total gas molecules); preferably, the content of impurities is lower than 1 ppb. Therefore, being able to measure in a precise and reproducible way extremely low impurity concentrations in gases is  
20   important.

          A technique that may be used for this purpose is ion mobility spectrometry, known in the filed under the acronym IMS; the same acronym is used also for the instrument by which the technique is carried out, in this case indicating “Ion Mobility Spectrometer”. The interest for this technique derives from its extremely  
25   high sensibility, which is accompanied by low size and cost of the instrument; by operating in suitable conditions, gaseous or vapor species in quantities of the order of the picograms (that is,  $10^{-12}$  g), or in concentrations of the order of parts per trillion (ppt, equivalent to a molecule of analyzed substance per  $10^{12}$  gas molecules of the sample) can be sensed in a gas medium. IMS instruments and  
30   methods of analysis wherein these are employed are described, for example, in US patents n. 5,457,316 and 5,955,886, in the name of the US company PCP Inc. and

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in US patent 6,229,143 and in the PCT patent application publications WO 02/40984, WO 02/052255 and WO 02/054058 in the name of the applicant.

The chemical and physical principles of the technique, as well as the interpretation of the IMS analysis results, are very complex. For an explanation of these principles and results, reference can be made to the book "Ion Mobility Spectrometry", edited by G. A. Eiceman and Z. Karpas and published in 1994 by CRC Press.

Briefly, an IMS instrument is essentially formed of a reaction zone, a separation zone and a charged particles collector.

10 The ionization of the sample, which comprises the gases or vapors to be analyzed in a transport gas, takes place in the reaction zone, commonly by means of beta radiations emitted by  $^{63}\text{Ni}$ . The ionization involves mainly the transport gas with the formation of the so-called "reagent ions", whose charge is then distributed on the present species as a function of their electron or proton affinities or of the ionization potentials thereof.

15 The reaction zone is divided from the separation zone by a grid which, when kept at a suitable potential, prevents the ions produced in the reaction zone from entering the separation zone. The instant when the grid potential is annulled, allowing entrance of the ions into the separation zone, gives the "time zero" of the analysis.

20 The separation zone comprises a series of electrodes which create an electric field suitable for transporting the ions towards a collector. In this zone, maintained at atmospheric pressure, is provided a gas flow having opposite direction with respect to that of ions movement. The counterflow gas (defined in the field as "drift gas") is an extremely pure gas, which can correspond to the gas whose impurity content has to be determined or a different gas. The speed of motion of the ions depends on the electric field and on the cross-section thereof in the gas medium, so that different ions take different times to cross the separation zone and reach on the particle collector. The time between the "time zero" and the arrival on the particle collector is defined "time of flight". The collector is connected to the signal elaboration system, which transforms the current values sensed as a

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function of time into the final graph, wherein peaks corresponding to the various ions as a function of the "time of flight" are shown; from the determination of this time, knowing the test conditions it is possible to determine the presence of the substances which are the object of the analysis, whereas from the peaks area by  
5 means of suitable calculation algorithms it is possible to calculate the concentration of the corresponding species.

However, the inventors have found that it is impossible to carry out an analysis of oxygen and water in hydrogen by the IMS technique according to the above mentioned principles.

10 During their experimental work, the inventors have found first of all that in order to carry out this analysis it is necessary to use as drift a rare gas selected amongst neon, argon, krypton and xenon, because by using pure hydrogen (that is, the pure gas corresponding to the one in which the impurities have to be determined) there is no peak separation; among the cited rare gases preferred is  
15 argon, since it is the one that provides the best results at a reduced cost. In these conditions, the  $H^+$  ions formed by the ionizing member combine with an argon atom, forming the species  $ArH^+$  (or other more complex species therefrom derived by combination of other argon atoms or other neutral molecules), which is the actual reactant species in this analysis. The  $ArH^+$  species transfers its charge with  
20 good efficiency to molecules such as nitrogen,  $N_2$ , carbon oxides, CO and  $CO_2$ , and particularly with excellent efficiency to the water molecule,  $H_2O$ , so that these impurities when present in hydrogen are easily identified in the IMS analysis. On the contrary, it has been observed that the efficiency of the reaction of charge transfer from  $ArH^+$  to the oxygen molecule,  $O_2$ , is nearly zero, so that in the  
25 spectrum resulting from the IMS hydrogen analysis there is no peak corresponding to oxygen; as a consequence, the presence of oxygen is not sensed, not even qualitatively, in this analysis.

Object of the present invention is providing a method and a system for measuring the concentration of oxygen and water in hydrogen by means of  
30 ionization mobility spectrometry.

These objects are achieved according to the present invention, which in a

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first aspect thereof consists in a method comprising the following steps:

a) carrying out a first measure of the water concentration in a hydrogen sample to be analyzed from which oxygen and water have been removed, in order to determine the contribution to the measure of water due to the "background" of the instrument;

b) carrying out a second measure of the water concentration in the same hydrogen sample from which water and optionally other impurities, but not oxygen, have been removed;

c) carrying out a third measure of the water concentration in the same hydrogen sample without any previous purification;

d) comparing the results of the three measures of steps a, b, c in order to determine independently the oxygen and water concentration in the hydrogen under analysis;

wherein all the above mentioned measures are made using in the separation zone of the IMS instrument a drift of a gas selected among neon, argon, krypton and xenon, and by operating in such a way that, at least in operations b and c, the sample of hydrogen under analysis is subjected, upstream of the IMS instrument, to an operation of conversion into water of the oxygen optionally present and such that in step b said conversion operation takes place subsequently to said water removal step.

The invention will be described in the following with reference to the figures, wherein:

- figure 1 schematically shows a system of gas lines comprising purifiers and a converter of oxygen into water for putting the method of the invention into practice;

- figure 2 shows the result of IMS hydrogen analyses corresponding to the different steps of the invention method.

In the course of the experiments, the inventors have carried out a number of tests with sample mixtures formed of hydrogen and known quantities of impurities such as nitrogen, methane, carbon oxides, water and oxygen. As already noted, while the other impurities give rise to peaks in the IMS spectrum,

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no peak is observed in the case of oxygen, even when this impurity is present in relatively high concentrations. The inventors have however noted that with increasing oxygen concentration in the hydrogen sample entering the instrument, the intensity of the water peak increases. This increase is however not linear with the oxygen concentration of the entering gas; besides, this increase is not reproducible in different IMS instruments, or even in subsequent measures carried out with the same instrument.

Although the phenomenon has not been completely explained, it is believed that a partial conversion of oxygen into water occurs inside the instrument, depending on the working conditions of the instrument, on the test temperature (which can vary between about 80 and 120 °C), and also as a consequence of a possible catalytic effect by the same instrument walls. Since the degree of this conversion is unforeseeable, it follows that a portion of the oxygen remains as a molecular species and therefore is not sensed in the analysis, whereas another portion is converted into water and causes an increase of the intensity of the relevant peak, thus altering the reading of the concentration of this species.

The method according to the invention solves these problems, allowing the measure of oxygen and water in hydrogen, both quantitative and qualitative, to be obtained with the IMS technique.

Since water is always present as "background" in an IMS measure (due to the slow water desorption from the instrument walls), the first step of the method of the invention, **a**, consists in evaluating the amount of this "background" so that it can be considered in the following measures. This is carried out by means of a first IMS analysis of the hydrogen sample, having previously subjected this hydrogen sample to an oxygen and water removal step: in this way the water which is determined in this first test is only that due to the "background", without contribution of the inlet gas. The oxygen and water removal can be made with gas purifiers generally known in the field, examples of which are described later.

In the second step of the method according to the invention, **b**, a second IMS measure of water concentration in a sample of the same hydrogen is carried out, by subjecting it first to a partial purification step, wherein water and

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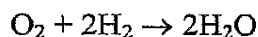
optionally also other impurities except oxygen are removed from the gas, and then to a step of conversion of oxygen into water. In this way the quantity of water which is determined in this second test is formed of the water derived from oxygen and of the "background" water.

- 5        In the third step of the invention method, **c**, a third measure of the water concentration is carried out in a sample of the same hydrogen, which is not subjected to any previous purification, but is subjected to the step of conversion of oxygen into water before being inlet into the IMS instrument. In this test, the quantity of water which is measured is formed of the three contributions, that is  
10    the "background" water, that formed by the oxygen present in the hydrogen as impurity and that originally present as an impurity in the hydrogen.

- The last step of the method, **d**, consists in comparing the results of the three measures of the steps **a**, **b** and **c** for determining independently the concentration of oxygen and water in the hydrogen under analysis. In particular, by indicating  
15    the results of the water concentration measures obtained in the three tests with  $[H_2O]_a$ ,  $[H_2O]_b$  and  $[H_2O]_c$ , it follows that:

$[H_2O]_a$  is equal to the water "background" of the instrument;

- the value deriving from the subtraction  $[H_2O]_b - [H_2O]_c$  is the water concentration deriving from the oxygen present in the initial hydrogen sample;  
20    given the reaction stoichiometry:



      the concentration of the oxygen originally present in the hydrogen sample is obtained, which will be half of the water concentration obtained from the above given subtraction;

- 25        finally, the value calculated from the subtraction  $[H_2O]_c - \{[H_2O]_b + [H_2O]_a\}$  provides the value of the water concentration originally present as impurity in the hydrogen sample.

- Obviously, steps **a**, **b** and **c** can be carried out as well in a different time order with respect to the above indicated one; similarly, the calculations given for  
30    step **d** can be made at different times, for instance all together at the end of the series of steps **a**, **b** and **c**, or the first subtraction step (by which the water



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concentration deriving from oxygen is obtained) can be carried out after test b, and the last subtraction operation (by which the water quantity actually present as impurity in the initial sample is obtained) can be carried out at the end of the test series. Preferably, the calculation steps are carried out in an automated way, for instance by means of a microprocessor which can be the same that with suitable algorithms obtains the values  $[H_2O]_a$ ,  $[H_2O]_b$  and  $[H_2O]_c$  from the peak intensities in the spectrum.

In a second aspect thereof, the invention relates to a system which allows carrying out the above described method. This system comprises:

- 10 - an IMS spectrometer;
- a line for introducing the hydrogen sample to be analyzed into the system;
- at least one flow deviator member capable of redirecting the gas flow entering into the system along at least three secondary lines;
- a first secondary line on which a first gas purifier capable of removing oxygen and water present in the hydrogen flow is provided;
- 15 - a second secondary line on which a second gas purifier, capable of removing water and optionally other impurities except oxygen, is provided;
- a third secondary line;
- flow selection members, intended to direct the flow in the system along only one of said secondary lines at a time;
- 20 - at least one fitting member of the three secondary lines upstream or at the entrance of the IMS spectrometer;
- at least one converter capable of converting completely the oxygen into water, downstream of said second purifier and in a position such that the hydrogen flow in said third secondary line passes through said converter before the entrance into the spectrometer.
- 25

The system according to the invention allows various alternative embodiments.

For example, the three secondary lines may remain parallel until the entrance into the IMS instrument, where are joined by a fitting; in this embodiment two separate oxygen to water converters are necessary, on the second

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and third secondary lines. However, preferably said two converters are replaced by a single converter; in this case, at least said second and third secondary lines must be joined, by means of a suitable fitting member, into a single line upstream of the only converter; the first secondary line can be joined to this last line downstream of said converter, or upstream thereof; in this latter case, preferably the three secondary lines are joined into a single line by means of a single four-way fitting member, which can be a second flow deviator member similar to the one positioned upstream of the three secondary lines. The elements which allow selecting one of the secondary lines along which the flow can be directed in the system can be of various type: conveniently, on-off valves positioned on each of said secondary lines are employed.

Figure 1 shows the preferred embodiment of the invention, which employs a single oxygen to water converter and minimizes the number of fittings and weldings. System 10 comprises a line 11 for connecting the system to the line from which the gas under analysis comes and a member 12 for selectively deviating the gas flow entering from line 11 along one of the secondary lines 13, 13' or 13''. The three secondary lines are then joined together, by means of a fitting member 12' in a single line 14 upstream of the IMS instrument 15. An on-off valve, 16, 16' and 16'', is positioned on each of the three secondary lines; by opening only one of these valves at a time, the secondary line along which the gas flow which is then sent to the IMS instrument is selected; the three valves are shown in the figure immediately upstream of member 12', but they could be positioned at any point of the secondary line. Along a first secondary line, 13, a first purifier 17 is positioned, capable of removing oxygen and water from the hydrogen flow which passes through the same line; along a second secondary line, 13', a second purifier 18 is positioned, capable of removing water and optionally other impurities except oxygen from the hydrogen flow passing through line 13'; finally, on line 13'' there is no purifier. The oxygen to water converter 19 is positioned along line 14.

The method according to the invention is carried out with system 10 by suitably operating valves 16, 16' and 16'' in such a way that the flow of only one

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of the secondary lines is sent alternatively to instrument 15; in particular, step **a** is carried out by sending to the instrument the flow coming from line 13, step **b** is carried out by sending to the instrument the flow coming from line 13' and step **c** by sending to the instrument the flow of line 13''.

5           System 10 is produced with standard materials and techniques in the field of ultrapure gases lines, for example by using steel pipelines for the gas lines, steel valves, and by subjecting the system to degassing treatments through heating, before setting it to work.

10           Purifier 17 can be of the palladium membrane type, but for economical reasons it is preferable to use nickel-based purifiers, which work at room temperature. In these purifiers the metal is generally present in the form of a deposit on a support having a high specific surface, such as silica; nickel-based purifiers of this kind are produced for example by the company SAES Pure Gas of San Luis Obispo, USA.

15           Purifier 18 must be capable of removing water and optionally other impurity except oxygen. For example, it is possible to use purifiers based on zeolites, which by working at temperatures comprised between about -50 °C and room temperature are capable of removing water and other easily condensable impurities, such as CO<sub>2</sub>, but not oxygen. It is also possible to use purifiers based  
20           on chemical moisture sorbers, working at room temperature; some examples are the purifiers based on boron oxide, capable of selectively removing water, or those based on the alkaline-earth metal oxides, capable of effectively removing water and, following to this sorption, also CO<sub>2</sub>; for economical reasons, the preferred alkaline-earth metal oxide is calcium oxide. These purifiers are formed  
25           of a body generally made of steel provided with two fittings for the connection (at the inlet and outlet) to the gas line, and, inside the body, the moisture sorbing material, generally in divided form (for example, powder) and retained by nets or metal filters, in order to avoid that particles of the material are transported downstream the purifier by the gas flow. Zeolites for use in these purifiers are  
30           commercially available, for example by the US company Grace Davison, Baltimore, Maryland, or by the French company CECA, Paris La Defence; the

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alkaline-earth metal and boron oxides are sold by any chemical products retailers, such as for example Aldrich, Merck, etc.; the use of boron oxide as moisture sorber is described in patent US 6,304,367 in the name of the Applicant.

Converter 19 must be capable of completely converting oxygen into water.

5 This converter has a similar construction to that of purifier 18, with a metal body wherein is contained a material active in the conversion, generally a transition metal in the form of a net, a sponge or deposited on a support in divided form, such as the ceramics or zeolite supports used in the catalytic applications. Preferred is the use of converters containing catalytic beds of palladium or, for

10 economical reasons, of nickel; in the latter case it is possible to employ nickel in the form of a net or sponge, and the conversion occurs at temperatures higher than 100 °C. Nickel in the form of sponge useful for the purposes of the invention is sold for example by the company INCO of Swansea, Wales, UK.

The invention will be further illustrated by means of the following

15 examples. The tests results are given in graphs wherein peaks in function of the time of flight of the ions in milliseconds (ms) are shown; the peaks have an area corresponding to the concentration of the different ions. These ions are in general complex species, which may comprise one, two or more molecules of ionized gas, optionally associated to more molecules of the transport gas, but for the sake of

20 simplicity the main peaks in the figures are identified with simplified formulas of a molecular species to which they are attributable, instead of the actual formula of the corresponding ion; for example, in the figures H<sub>2</sub>O indicates ions attributable to the presence of water, (H<sub>2</sub>O)<sub>2</sub> indicates ions corresponding to ions containing a water dimer, whereas RIP indicates the reactant ion, that is ArH<sup>+</sup>. The intensity of

25 the peaks is given in volts (V); the transformation into volts of the current directly measured by the collector (number of ions which collide on the collector in the time unit) is carried out by the instrument electronics. The sample ionization is obtained through a radioactive source of <sup>63</sup>Ni. The separation zone of the instrument used is 8 cm long; in all the tests the electric field applied is 128V/cm.

30

#### EXAMPLE 1

This example is illustrative of the carrying out of operation a of the method

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according to the invention.

An IMS analysis of a hydrogen sample from which all the impurities have been removed is carried out for determining the contribution to the water measure of the background of the system. The test is carried out using the system of figure 1, by passing through line 13, on which purifier 17 is provided, a gas mixture obtained by adding 5 ppb of water (by means of a calibration system of the company KIN-TEK of LaMarque, Texas, USA) to hydrogen comprising 5 ppb of oxygen (provided by the company SIAD of Bergamo, Italy); due to the configuration of system 10 the gas flow deriving from the purification step passes through the converter of oxygen into water, 19, even if this last step would not be necessary in this case, and finally sent to the IMS instrument 15. The temperature in the instrument is kept constant at 100 °C and pure argon is used as drift gas, with a flow ratio between the sample and the drift gas of 1.2 : 20. The test result is given in figure 2 as curve a.

#### 15 **EXAMPLE 2**

This example is illustrative of the carrying out of step b of the method according to the invention.

The test of example 1 is repeated, but sending to the IMS instrument the gas derived from the starting mixture which has been passed through line 13', from which therefore only water has been removed, and then through converter 19. The result of the test is given in figure 2 as curve b.

#### **EXAMPLE 3**

This example is illustrative of the carrying out of step c of the method according to the invention.

25 The test of example 1 is repeated, but sending to the IMS instrument the starting mixture which has been passed through line 13'', thus without any purification step, and then through converter 19. The result of the test is given in figure 2 as curve c.

30 As noted from the analysis of the graphs in figure 2, passing from condition a to c the intensities of the peaks attributable to water and to its dimer regularly increase, whereas the intensity of the reactant ion decreases.

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In the first test the calculation algorithm of the system determinates a water concentration equal to 3.1 ppb, which represents the "background" of the system.

In the second test, the measured value by the instrument is 11.6 ppb, from which by subtraction of the background a value of 8.5 ppb of water can be  
5 obtained: considering that 5 ppb of oxygen have been sent to the instrument, which have given by conversion 10 ppb of water, in this case a "reading" of the instrument 15% lower than the correct value is obtained, that is an acceptable value at these values of concentration of impurities.

Finally, in the third test all the contributions are present, that is the  
10 "background", the water derived from oxygen conversion and that originally present in the hydrogen sample; the "reading" of the instrument in this case is 18.3 ppb from which, by subtracting 3.1 ppb of the "background" and the 10 ppb of water derived from oxygen, a reading of water of 5.2 ppb is obtained, with an error of 4% in excess with respect to the correct one, which is an excellent result.

15 The method and the system according to the invention allow therefore to determine with good reliability, independently from one another, the concentrations of oxygen and water in a hydrogen sample.

## CLAIMS

1. A method for measuring the concentration of oxygen and water in  
5 hydrogen by means of ion mobility spectrometry comprising the following steps:
- a) carrying out a first measure of water concentration in a sample of hydrogen  
to be analyzed from which oxygen and water have been removed, in order to  
determine the contribution to the measure of water due to the "background"  
of the instrument;
  - 10 b) carrying out a second measure of water concentration in a sample of the  
same hydrogen from which water and optionally other impurities, but not  
oxygen, have been removed;
  - c) carrying out a third measure of water concentration in a sample of the same  
hydrogen without any previous purification; and
  - 15 d) comparing the results of the three measures of steps **a**, **b** and **c** in order to  
determine independently the concentration of oxygen and water in the  
hydrogen under analysis;
- wherein all the above mentioned measures are made using in the separation zone  
of the IMS instrument a drift of a gas selected among neon, argon, krypton and  
20 xenon, and by operating in such a way that, at least in operations **b** and **c**, the  
sample of hydrogen under analysis is subjected, upstream of the IMS instrument,  
to an operation of conversion into water of the oxygen optionally present and such  
that in step **b** said conversion operation takes place subsequently to said water  
removal step.
- 25 2. A method according to claim 1 wherein the steps for comparing the  
results of the three measures are carried out in an automated way by means of a  
microprocessor.
3. A method according to claim 1 wherein said drift gas is argon.
4. A system for measuring the concentration of oxygen and water in  
30 hydrogen by means of ion mobility spectrometry comprising:
- an IMS spectrometer (15);

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- a line (11) for introducing the hydrogen sample to be analyzed into the system;
- at least one flow deviator member (12) capable of directing the flow of the gas entering into the system along at least three secondary lines;
- a first secondary line (13) on which a first gas purifier (17) is positioned,  
5 capable of removing oxygen and water present in the hydrogen flow;
- a second secondary line (13') on which a second gas purifier (18) is positioned, capable of removing water and optionally other impurities, but not oxygen, from the hydrogen flow;
- a third secondary line (13'');
- 10 - flow selection members, for directing the flow in the system along only one of said secondary lines at a time;
- at least one fitting member (12') of the three secondary lines upstream or at the entrance of the IMS spectrometer (15);
- at least one converter (19) capable of converting completely oxygen into  
15 water, downstream of said second purifier (18) and in a position such that the hydrogen flow in said third line (13'') passes through said converter before entering into the spectrometer.

5. A system according to claim 4, wherein the second (13') and the third (13'') of said secondary lines are joined into a single line by means of a fitting  
20 member, and wherein between said fitting member and the IMS spectrometer is positioned a single converter (19) of oxygen into water.

6. A system (10) according to claim 5, wherein all the secondary lines (13, 13', 13'') are joined into a single line (14) by means of a fitting member (12') and  
25 wherein the single converter (19) is positioned between said fitting member and the IMS spectrometer.

7. A system according to claim 6, wherein the flow selection members are on-off valves (16, 16', 16'') positioned on each of said three secondary lines (13, 13', 13'').

8. A system according to claim 4 wherein said first purifier (17) positioned  
30 on said first secondary line (13) contains nickel.

9. A system according to claim 8, wherein nickel is in the form of a deposit



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on a support having a high specific surface.

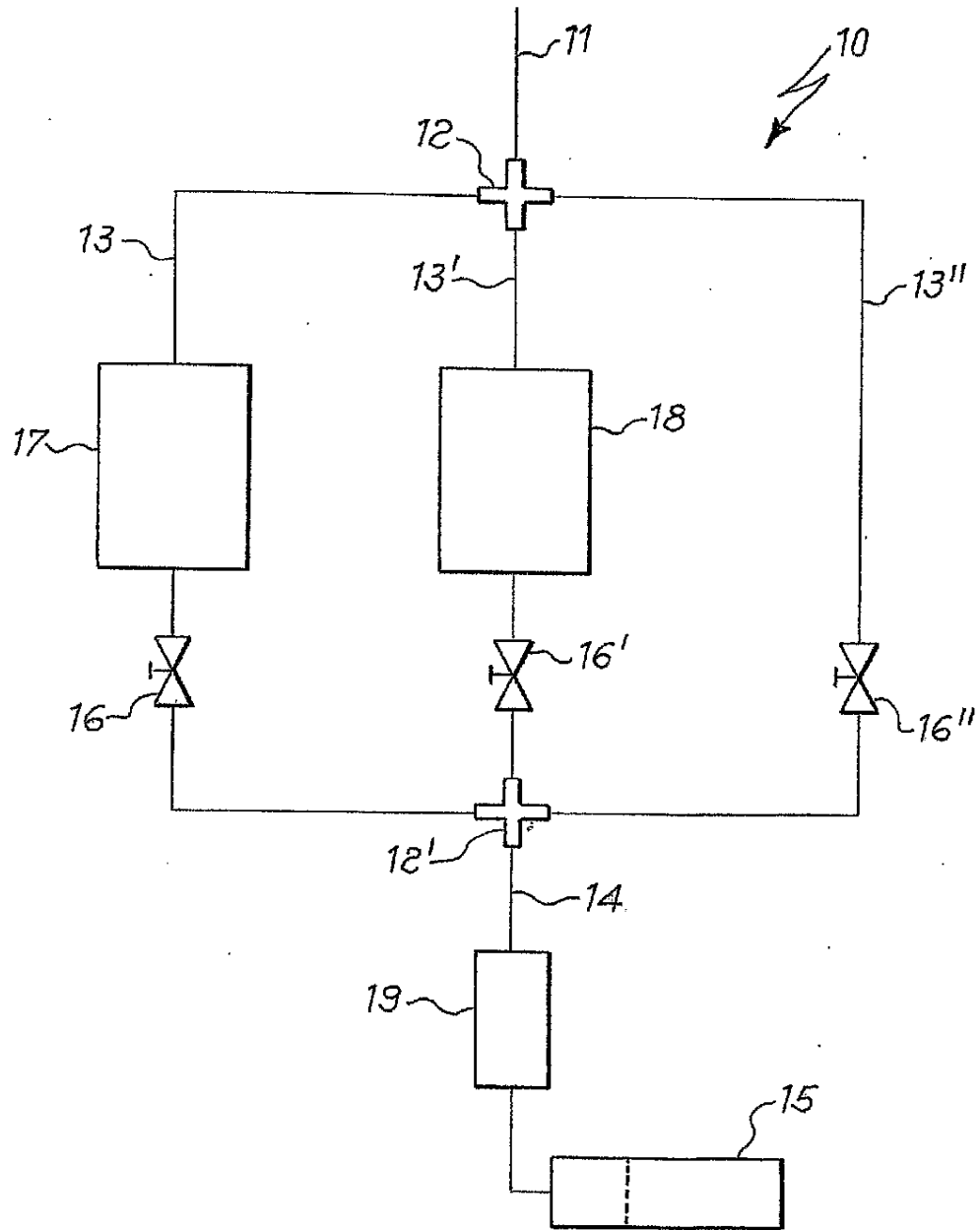
10. A system according to claim 4 wherein said second purifier (18) positioned on said second secondary line contains zeolites.

11. A system according to claim 4 wherein said second purifier (18)  
5 positioned on said second secondary line contains a chemical moisture sorber.

12. A system according to claim 11 wherein said chemical moisture sorber is calcium oxide.

13. A system according to claim 4, wherein said converter of oxygen into water contains nickel.

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Fig. 1

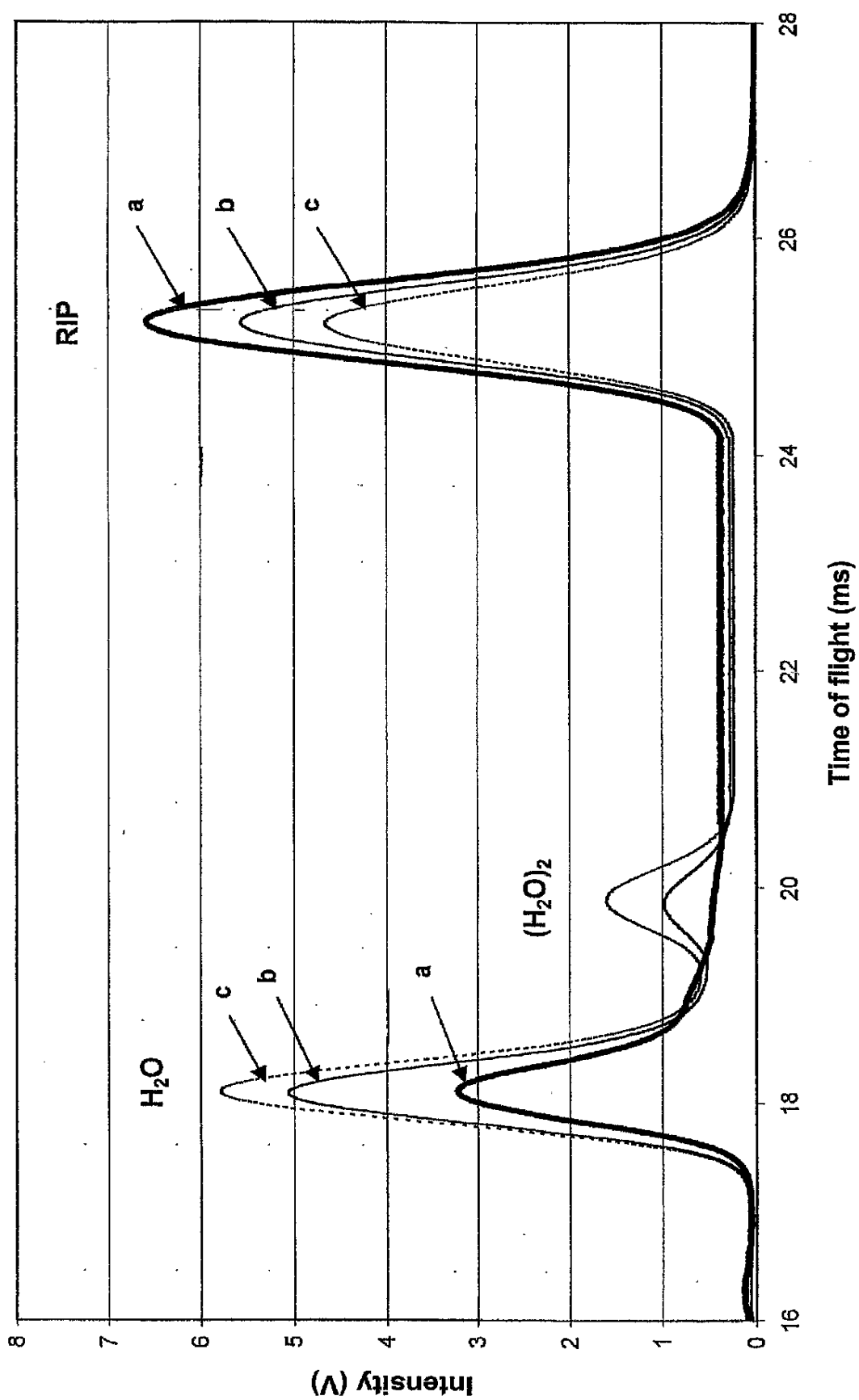


Fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IT 03/00550

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 G01N27/64 G01N33/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 098 650 A (SAYLES DONALD A) 4 July 1978 (1978-07-04) abstract; figure 2 ---	1, 4
A	WO 02 052255 A (GETTERS SPA ;PUSTERLA LUCA (IT); SUCCI MARCO (IT); BONUCCI ANTONIO) 4 July 2002 (2002-07-04) cited in the application claim 1 ---	1, 4
A	GB 1 225 075 A (WESTINGHOUSE ELECTRIC CORP.) 17 March 1971 (1971-03-17) page 3, line 35 - line 53; figure 10 ---	1
A	US 5 138 869 A (TOM GLENN M) 18 August 1992 (1992-08-18) column 6, line 8 -column 7, line 57; figure 1 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \* & \* document member of the same patent family

Date of the actual completion of the international search

15 December 2003

Date of mailing of the international search report

29/12/2003

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 304 752 A (JENKINS ANTHONY ET AL) 8 December 1981 (1981-12-08) abstract -----	1

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Information on patent family members

International Application No

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